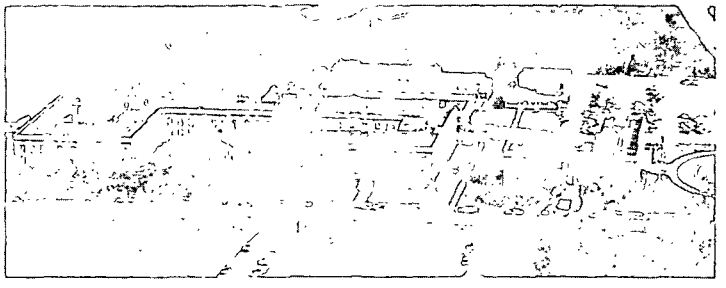

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SUMMARY

Color removal is a pollution problem which is particularly difficult to treat due to the dilute nature of the effluent. Most of the color is derived from the pulp washings and the caustic extract stage of bleaching. This paper describes a laboratory study of a new method of removing color from such effluents, using polyamines to precipitate the color bodies. The precipitates appear to be easily dewatered, offering a distinct advantage over lime precipitation. A survey of several polyamines is given, and several experiments aimed at elucidating the mechanism of precipitation are reported.

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Color Removal from Softwood Kraft Caustic Extract by Polyamines

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ABSTRACT

Color bodies from a freeze-dried, softwood kraft caustic extract effluent and from a partially purified, acid-precipitated color body fraction (Fraction I) were found to precipitate when treated with polyamines. Against caustic extract effluent color, each polyamine had a pH range yielding optimal color removal. The largest polymer studied, PEI 18 (a branched polymer of ethyleneimine $\overline{M}_n$ 1,800 $\pm$ 300), was the most effective precipitant, achieving 85 to 90% color removal at pH 7 to 8.5 and polyamine concentrations of 550 to 800 ppm. Lower molecular weight branched polyamines (tetraethylenepentamine to ethylenediamine) were less effective. Fraction I color bodies were far more easily precipitated. Color removal and precipitate composition were found to be dependent upon both the cationic character of the polyamine and the anionic character of the color bodies. The precipitate retained the ionic character of the reacting species, and contained only small amounts of inorganic counterions. Conductivity and zeta potential measurements were used to probe the mechanism of precipitation from Fraction I, and a general mechanism was proposed, involving a rapid initial interaction based on coulombic attraction, which ultimately leads to the formation of larger aggregates which precipitate.

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Color Removal from Softwood Kraft Caustic Extract by Polyamines

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In recent years the pulp and paper industry has markedly improved the quality of effluents discharged to the aqueous environment. However, one of the most difficult environmental problems, that of removing effluent color, remains to be adequately solved. In bleached kraft mills, 60 to 70% of the total color is typically derived from one effluent stream, the first caustic extract after chlorination (1,2). A variety of methods for removing color from caustic extract effluents have been shown to be fairly effective in some situations. These include precipitation by di- and trivalent metal cations (3,4), ion exchange (5), adsorption by activated charcoal (6) or synthetic resins (7), reverse osmosis (8), chemical (9) or photochemical oxidation (10), and phase separation using long chain aliphatic amines, emulsified in hydrocarbon solvents (11).

This work presents a new method for removing soluble color: the precipitation of color bodies by polyamines. The polyamines studied were PEI 18, 12 and 6 (branched polymers of ethyleneimine, M_n 1,800 ± 300, 1,200 ± 200, and 600 ± 100, respectively), tetraethylenepentamine, triethylenetetramine, diethylenetriamine, ethylenediamine and its symmetrical N-methyl-substituted analogs (di- through hexamethyl), 1,3-diaminopropane, 1,4-diaminobutane, 1,12-diaminododecane and ethylamine.

RESULTS

Table 1 shows the color removals obtained from several caustic extract effluents when treated with PEI 8 at pH 7. Color removal levels of 89 to 96% were obtained with all the effluents tested, although some variation in the PEI

18 requirement was noted. Precipitation was rapid and the dense precipitate formed appeared to have good settling properties. In order to gain further insight into the factors which are important in precipitation, Mill A effluent was selected for study, and freeze-dried for use as a caustic extract standard (CES).

(Table 1 here)

Color Removal from CES

Color removal from CES by PEI 18 at several pH's is shown in Fig. 1. This polyamine was the most effective precipitant, achieving 85 to 90% color removal at the optimum pH range of 7 to 8.5, at PEI 18 concentrations of 12 to 18 milliequivalents of nitrogen per liter (meq N/liter), i.e., 550 to 800 ppm. Under these conditions, the addition of PEI 18 caused an instantaneous turbidity, followed by the formation of a dense precipitate which settled rapidly. Color removal was dependent upon both the pH of the precipitation medium and the polyamine concentration. When the PEI 18 was in excess of that required to achieve maximum color reduction, the percent color removal observed decreased. These nonoptimal conditions produced a suspended precipitate, which settled only slowly. Color removal by PEI 12 and 6 showed a trend toward higher pH optima, higher optimum polyamine concentrations, and lower color removal.

The low molecular weight linear polyamines also removed CES color, but less effectively than PEI 18. As before, color removal showed an optimum pH range (Table 2), but the optima occurred at acidic conditions and decreased with decreasing molecular weight, as did the ultimate color removal levels observed (Table 2). The presence of excess polyamine had little effect on maximum color removal, as shown in Fig. 1. However the rate of precipitation increased with increasing polyamine concentration.

(Table 2 and Fig. 1 here)

Of the diamines tested, only ethylenediamine and 1,12-diaminododecane removed color. Ethylenediamine was weakly effective, removing about 20% of CES color at concentrations of 40 meq N/liter or more at pH's 4 and below. In contrast, 1,12-diaminododecane was able to achieve over 70% color removal at concentrations of about 20 meq N/liter at pH's 8 and below. The greater color removal observed for 1,12-diaminododecane was attributed, at least in part, to differences in polyamine-solvent(water) interactions resulting from the presence of the twelve carbon chain and no attempt was made to correlate its effects with those of the other polyamines.

Polyamine Protonation at Optimum pH

The degree of protonation at optimum pH was determined by titration for several of the polyamines of interest (Table 2). For di- and triamines the pH optima corresponded to completely or nearly completely protonated species. Triethylenetetramine produced maximum color removal at 75% protonation, i.e., three cationic sites per molecule. With tetraethylenepentamine, maximum color removal occurred at 60% protonation, which also corresponds to three cationic sites per molecule. The pH optima for the PEI series occurred at percent protonations of 35 to 50%. Thus, the trend established is that dications can remove CES color but triprotonated species are more effective. When the number of potential cationic sites exceeds three, color removal is favored by increasing charge separation until an apparent optimum separation is reached. While these data indicated that the cationic character of the polyamine was important in the precipitation, very little could be inferred about the role of the color bodies. To obtain a clearer view of the role of color bodies in precipitation, color removal was also studied using a partially purified, more readily precipitated color body fraction obtained from CES by acid precipitation. This material (Fraction I) represented 40% of the original CES color and about 10% of the initial solids. Fraction I color bodies had higher molecular weights and were less acidic than the average CES color bodies.

Color Removal from Fraction I

Fraction I color bodies were far more easily precipitated than those of CES. When PEI 18 was tested, color reductions of 95% or more were observed at pH's between 4 and 9. Both PEI 12 and 6 showed similar levels of color removal. The effect of decreasing pH was to decrease the solution concentrations of the polyamines required to achieve these levels. The effect of excess polyamine varied. With PEI 18 at pH's 4 through 9, or PEI 12 at pH's 8 and below, excess polyamine decreased color removal sharply, as shown in Fig. 2. With PEI 6, or PEI 12 at pH 9, the color removal profiles were relatively unaffected by excess polyamine, showing that the shape of the color removal curve was dependent upon the number of cationic sites per molecule. When tetraethylenepentamine was the precipitant, over 90% color removal was observed at pH 7 (Fig. 2) and below. Excess polyamine had no effect on the ultimate color removal level. In contrast, color removal by diethylenetriamine was strongly dependent upon the pH of the precipitation medium. At pH 7, where the triamine was doubly protonated, only 50% color removal was produced at concentrations of 30 meq N/liter or more. As the pH decreased, increasing the cationic character of the triamine, color removal increased; at pH 4, 3 meq N/liter gave about 91% color removal.

(Fig. 2 here)

Precipitate Polyamine Content

The polyamine content of several CES and Fraction I precipitates was determined directly by total nitrogen analysis of the precipitates, and by difference, using a spectrophotometric method for determining supernate polyamine concentration. When both methods were applied to the same samples, the results were in agreement. When the composition of CES and Fraction I precipitates were normalized and compared, color removal by the linear polyamines was roughly proportional to both precipitate dry weight and polyamine content. When the normalized PEI 18 precipitate compositions were compared, it was evident that the PEI 18-CES precipitate contained far more PEI 18 per unit of color removed than

from Fraction I. Therefore, color removal from CES involved the precipitation of at least two types of color bodies; those typified by Fraction I, which could be precipitated by all of the polyamines, and those species soluble at pH 1, which were precipitated only by the larger branched PEI's.

When the polyamine contents of various Fraction I precipitates were compared on the common basis of milliequivalents of ammonium ion, using the ionic character of the amine in solution, as determined by titration, the values were approximately constant at each pH (Table 3). The amount of polyamine in the precipitate appeared to be directly proportional to the cationic character of the polyamine in solution. Table 3 also shows that as the pH of the precipitation medium increased, the polyamine ammonium ion equivalents increased. Since the anionic character of the color body fraction in solution increased with increasing pH (Table 3), it is reasonable to conclude that the polyamine content of the precipitate was also dependent upon the anionic character of color bodies. As can be seen, the increase in the number of anionic sites in Fraction I parallelled the increased in precipitate ammonium ion equivalents.

(Table 3 here)

The Ionic Character of the Precipitate

Infrared spectroscopy of the dry precipitates showed that the carboxyl/carboxylate ratio of the color bodies was the same before and after precipitation by polyamines. Hence, the precipitate retained the ionic character of the color bodies and presumably of the polyamines; proton transfer from a cationic group to carboxylate anion, to yield two uncharged species, was not extensive, if indeed it occurred at all.

Analysis of precipitate inorganic counterion content showed that the total sodium and chloride content was less than 7% of the ionic equivalents attributed to the color bodies and polyamines, showing that both localized and

overall electrical neutrality was achieved primarily through the association of color body anionic sites with polyamine cationic sites.

Conductivity and Zeta Potential Measurements.

The early stages of precipitation of Fraction I color bodies were examined by comparing the changes in conductivity as polyamines were added to Fraction I with the changes as polyamines were added to a KCl solution having the same inital pH and conductivity as Fraction I. The addition of either PEI 18 or tetraethylenepentamine increased the conductivity of Fraction I solutions, but the increase was significantly less than observed when these amines were added to the KCl solution. When ethylamine was added, the increase in conductivity was the same for both solutions. From these results, it was concluded that the polyamines complexed with Fraction I components, decreasing the number and/or effectiveness of the charge carrying species. Complexation was rapid, and could occur even at non-precipitating polyamine concentrations.

The latter stages of precipitation of Fraction I color bodies were examined by determining the zeta potential of precipitated particles. When either PEI 18 or tetraethylenepentamine was the precipitant, the particles formed on the initial portion of the color remaining curve showed negative zeta potentials (Fig. 2). As the PEI 18 concentration was increased, the zeta potentials became less negative, and passed through zero at maximum color removal. On the ascending portion of the color remaining curve, where PEI 18 was present in excess, positive zeta potentials were observed. In contrast, as tetraethylenepentamine concentration was increased beyond the point of increasing color removal, the zeta potentials of the particles remained slightly negative to zero, even in the presence of excess polyamine. When the order of addition was reversed, i.e., when color bodies were added to polyamine, the zeta potential of the precipitate showed the same behavior.

Thus, it was not possible to build up a positive surface charge when tetraethylenepentamine was the precipitant.

DISCUSSION

The Mechanism of Precipitation of Fraction I Color Bodies

The results obtained show that color removal involves interactions between the anionic color bodies and the cationic polyamines, and are consistent with the following general mechanism. At a given pH there are a number of anionic color body sites. As polyamine, at the reference pH, is added, a coulombic interaction leads to complex formation. The formation of the complex is rapid and occurs even at nonprecipitating polyamine concentrations. The complexation results in a decrease in the net negative charge on the color bodies. As more polyamine is added, the size of the complex increases and aggregates form. The addition of more polyamine promotes further aggregation, either by intimate association with a portion of the remaining anionic sites, or by depressing the electrical double layer in accord with the Derjaguin-Landau, Verwey-Overbeek (DLVO) theory of colloidal stability (13), thus enhancing the likelihood of aggregate association and subsequent precipitation. The precipitate retains the ionic character of the interacting species, and both overall and localized electrical neutrality are achieved primarily by the association of anionic color body sites with cationic polyamine sites.

As the number of cationic sites per polyamine molecule increases, color removal increases and the solution concentration required to achieve maximum color removal decreases. The enhanced color removal must be attributed to the increasing cationic character of the polyamine. When the polyethyleneimines were the precipitants, color removal was more rapid than with the low molecular weight polyamines. These branched polyamines are larger and contain many more cationic sites per molecule. This would lead to larger initial complexes and

aggregates. The decrease in color removal when PEI 18 was present in excess can be attributed to the reversal of charge on the particles due to the binding of more than the stoichiometric amount of the cationic polyamine. The fact that no positively charged species were detected when tetraethylenepentamine was the precipitant shows that linear polyamines cannot be complexed in sufficient quantity to bring about charge reversal.

To determine whether color removal from Fraction I could be explained as a solubility product (K_{sp}) phenomenon, the effects of dilution on color removal by tetraethylenepentamine were determined. The concentration of tetraethylenepentamine required to either initiate or achieve maximum precipitation was found to decrease with Fraction I dilution. This observation suggests that color removal cannot be explained as a classical K_{sp} phenomenon.

The Mechanism of Color Removal from CES

There is evidence to suggest that the Fraction I mechanism can be extended to account for color removal from CES.

1. The relative order of effectiveness and qualitative rates of precipitation for the various polyamines were similar in both color body systems.

2. Both systems showed similar color removal profiles and enhanced precipitation when tricationic species were present.

3. The diethylenetriamine, pH 4, precipitates from CES and Fraction I showed similar nitrogen contents and color removal was proportional to precipitate dry weight. The same is true for tetraethylenepentamine at pH 5 with both color body systems.

Since both systems showed similar behavior, similar mechanisms are probably operative. However, some differences were also noted. These include:

1. The polyamine content of Fraction I-PEI 18 precipitates was much lower than that found in the CES-PEI 18 precipitates. These difference are reflected in the lack of proportionality between color removal and precipitate dry weights.

2. With CES, the polyamines showed definite pH optima, whereas this was not observed with Fraction I.

Presumably, a portion of these differences can be attributed to interactions with the soluble supernate components which were not present in the acid-precipitated material (Fraction I).

EXPERIMENTAL

CES was prepared by freeze-drying Mill A caustic extract after pressure filtration through a 0.45 μm Millipore Filter. It has been reported that freeze-drying had little effect on caustic extract color or sedimentation coefficient, even with long periods of storage (12). In reconstitution, a measured amount of CES was dissolved in distilled water. After 15-20 min of stirring, the pH of the sample was adjusted as desired and the sample was diluted to twice the original CES concentration, or 0.910 g/50 ml.

To determine color removal, an aliquot of this 2X CES solution was transferred to a sample tube containing a known amount of water, the solutions were mixed and the desired amount of polyamine, at the desired pH, was added with mixing. The pH was readjusted if required. In all cases the final volume was such that CES was at its original concentration (0.910 g/100 ml). The solutions were capped and stored in the dark at 20°C for 24 ± 1 hr. Then the samples were centrifuged and the absorbance of the supernate at 450 nm was determined. Data were expressed as percent of the original 450 nm absorbance remaining. Precipitates were washed with distilled water, freeze-dried and weights recorded.

Fraction I was obtained by acidifying a concentrated (9X) solution of CES to pH 1 with concentrated HCl. After 18 hr at 4°C, the precipitate was collected by centrifugation, resuspended in distilled water and freeze-dried. Reconstitution was as for CES except that NaOH was added to give pH 7 to 8 during the initial resolubilization. Color removal was determined as described above.

The total nitrogen content of precipitates was determined using a Coleman Nitrogen Analyzer. Supernate polyamine concentrations were determined using the method of Kindler (14), except that the optical density at 290 nm was followed and the samples were made 0.04M in lead acetate, pH 5.3, to prevent complexation of the color bodies with the cupric ion.

Zeta potentials were determined using a Model B, ZETAMETER, (Zetameter Inc., New York, NY).

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Table 1. Color Removal from Caustic Extract Effluents by PEI 18 at pH 7

Mill	Fiber source	Initial color (o.d. @ 450 nm)	Maximum color removal, %	PEI concentration required, ppm
A	Mixed softwood	3.2	89	600
B	Mixed softwood	4.0	96	400
C	ca. 95% softwood, 5% hardwood	4.6	95	800
D	70% softwood, 30% hardwood	3.1	92	200

Table 2. Polyamine Protonation at Optimum Color Removal

Polyamine	Maximum color removed, %	Optimum pH	Protonated sites per molecule at optimum pH	%
Ethylenediamine	20	4-3	2.0	(100)
Diethylenetriamine	50	4-3	2.6-2.9	(86-97)
Triethylenetetramine	60	5-4	2.7-3.3	(66-83)
Tetraethylenepentamine	70	6-5	2.9-3.2	(58-64)
PEI 6	75	9.0-8.5	4.6-6.1	(33-44)
PEI 12	85	8.5-7.5	10.5-14.7	(35-49)
PEI 18	89	8.5-7.0	13.8-20.5	(33-50)

Table 3. The Polyamine Content of Various Fraction I Precipitates[a]

	Protonatable groups[b] in Fraction I (meq/liter)	Milliequivalents of Ammonium Groups[c] in Precipitates from			
		PEI 18	tetraethylene-pentamine	diethylene-triamine	1,12-diamino-dodecane
pH 7	1.31	1.11	0.99	0.96	0.92
pH 6	1.08	0.90	0.88	--	--
pH 5	0.89	0.73	0.77	0.63	--
pH 4	0.58	0.67	0.61	0.62	0.66

[a] Normalized to 100% color removal from one liter of Fraction I.
[b] Assuming complete protonation at pH 2.
[c] Assuming the cationic character of the polyamine in solution.

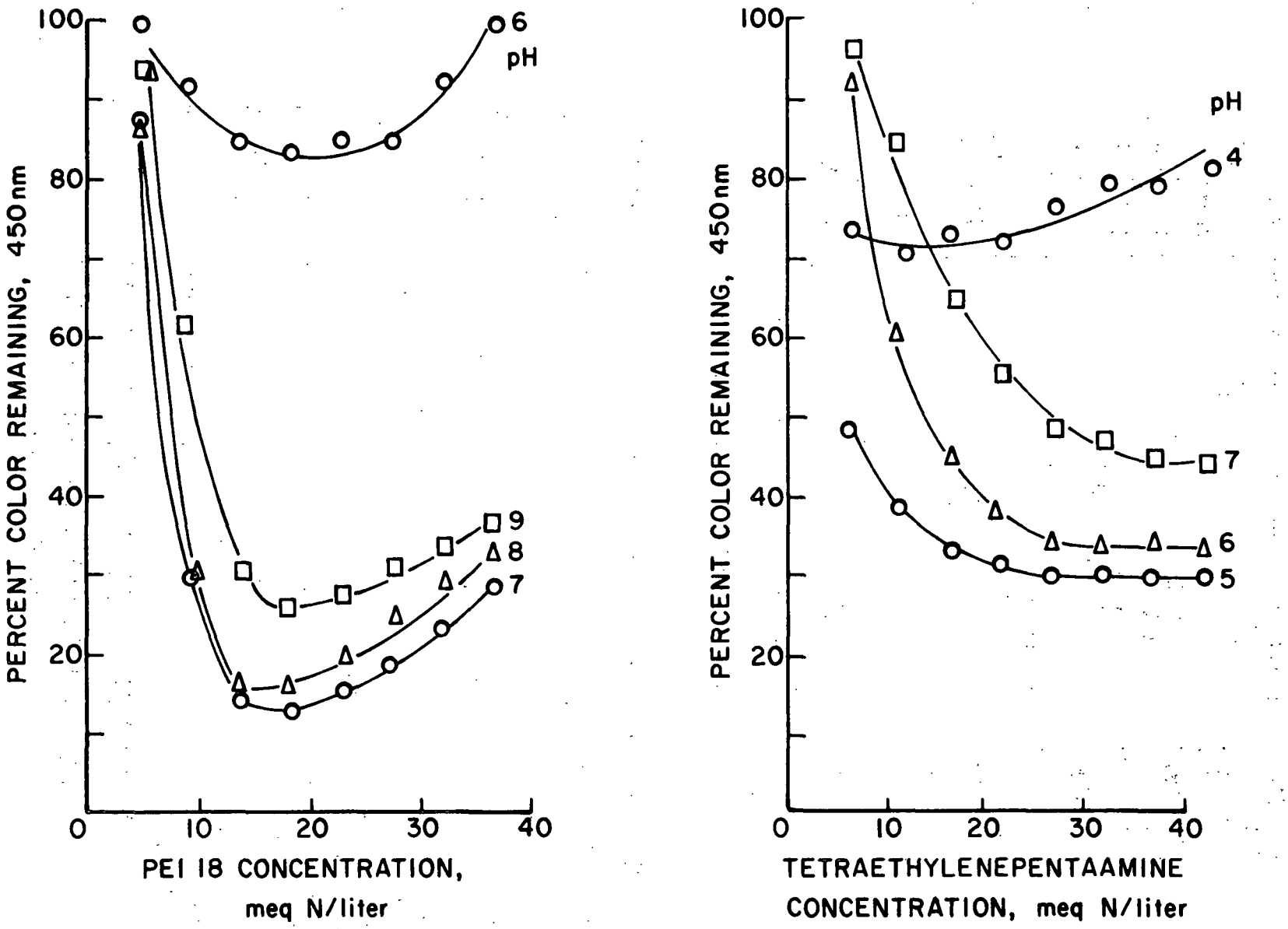
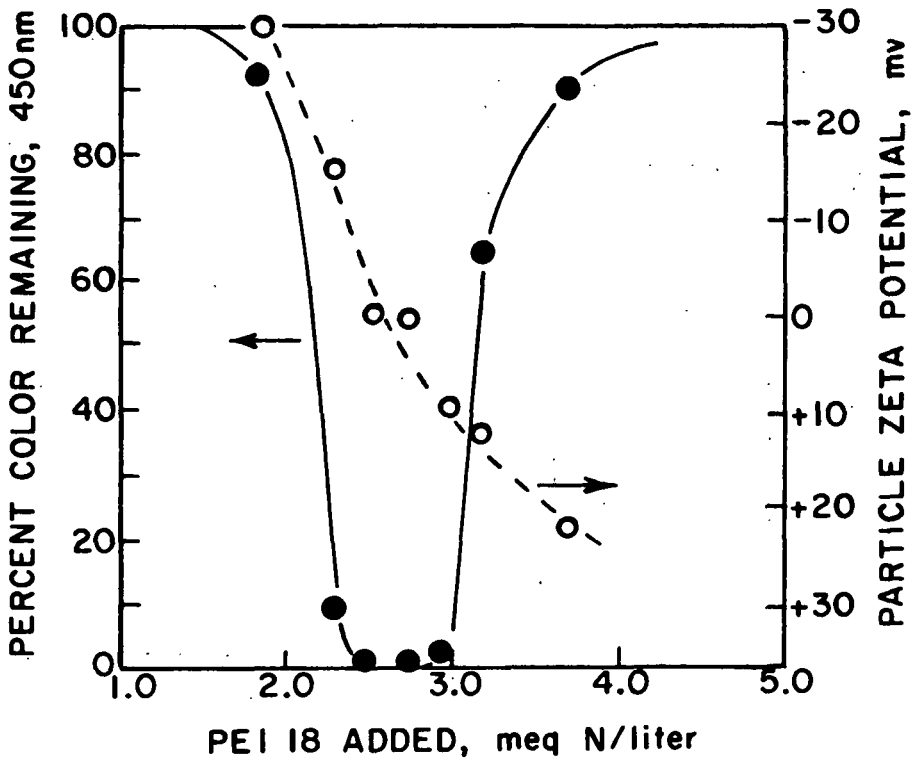


Fig. 1. Color removal from CES by PEI 18 and tetraethylenepentaamine



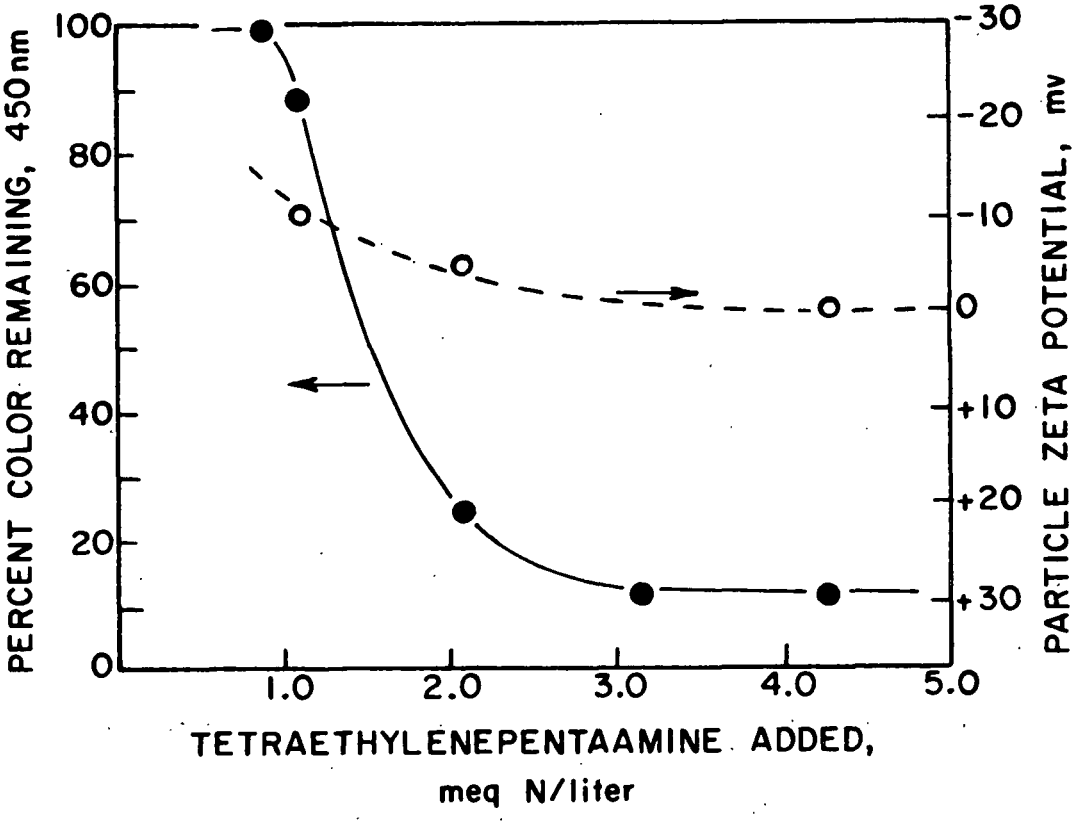


Fig. 2. Zeta potentials of Fraction I particles precipitated at pH 7